1,3-Dipolar cycloadditions of aldehydes or imines with carbonyl ylides generated from epoxides: classical heating and microwave irradiation

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Abstract—*Cycloadditions of aldehydes with carbonyl ylides to give dioxolanes have been carried out without solvent under microwave irradiation. The reactions proceeded in similar yields and stereoselectivities, but in shorter reaction times, than those obtained in toluene at reflux using an oil bath. Cycloadditions conducted between imines and carbonyl ylides using the same protocol were less efficient since the oxazolidines formed proved unstable under the reaction conditions.*

Keywords: 1,3-dipolar cycloaddition, microwave irradiation, dioxolanes, oxazolidines.

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1. Introduction

1,3-Dipolar cycloaddition reaction offers a versatile route for building five-membered heterocycles.[1] Among dipoles, carbonyl ylides generated from thermal electrocyclic ring opening of epoxides are known to undergo [3+2] cycloaddition with π-bonds to afford oxa-cyclic systems.[2]

A rising number of articles have advocated the use of microwave technology in organic synthesis. Harsh conditions such as high temperatures and long reaction times often required for cycloaddition reactions could generally be reduced using this technique.[3] In 2003 we have published the first microwave-induced syntheses of tetrahydrofurans using 1,3-dipolar cycloaddition reactions of alkenes with carbonyl ylides generated from epoxides.[4] In continuation of our investigation, we studied the syntheses of dioxolanes and oxazolidines using reactions of aldehydes and imines, respectively, instead of alkenes with the same 1,3-dipoles. We report here our results on the preparation of 2,4-disubstituted 1,3-dioxolane-5,5-dicarbonitriles and 2,3,4-trisubstituted 1,3-oxazolidine-5,5-dicarbonitriles under microwaves.

2. Results and discussion

The cycloaddition reactions between a series of aldehydes and carbonyl ylides generated in situ from the oxiranes **1** (X = H, Cl, OMe) were first attempted using different reaction conditions and methodologies. The best results were obtained using a solvent-free reaction coupled with microwave irradiation,[5] with reduction of reaction times in comparison to classical heating conditions.[2d,e]

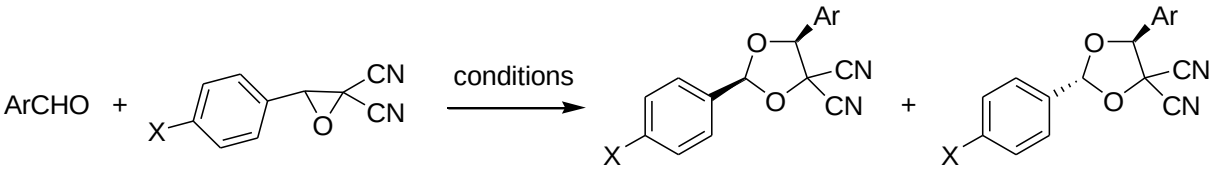
Several experiments were performed, at various powers and irradiation times, in order to find the most adequate conditions, which are presented in Table 1. Thus, the dioxolanes **2-3** have been prepared by irradiating the mixtures of aldehyde (3,4,5-trimethoxybenzaldehyde or piperonal) and epoxide for 30-45 min so as to keep the temperature of the reaction mixture at 80-120°C.

The reactions did not proceed when the reactants were heated without solvent in an oil bath, because of the more rapid decomposition of epoxides. The use of toluene at reflux afforded the dioxolanes **2-3** in similar yields, but after 35 to 72 h of stirring, depending on the electron-

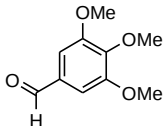
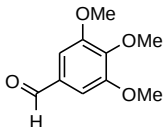
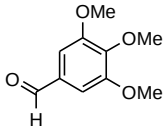
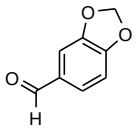
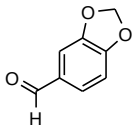
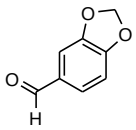
donating ability of the group present at the *para*-position on the phenyl ring of the epoxide. Indeed, it has been previously observed that the reactivity of the epoxide varies in the order **1-OMe** >> **1-H** ~ **1-Cl**.[2d,e]

The diastereoisomeric ratios in the mixtures were determined from ^{1}H NMR spectral analysis, and the *cis*- and *trans*-products were identified on the basis of their ^{1}H and ^{13}C NMR spectra, and in comparison with the literature data.[2d,e] The ratios proved to be similar using classical heating and microwave irradiation, with the *cis* isomer being the major product.

Table 1. Reactions between benzaldehydes and epoxides to give 1,3-dioxolanes



1 **a** **b**

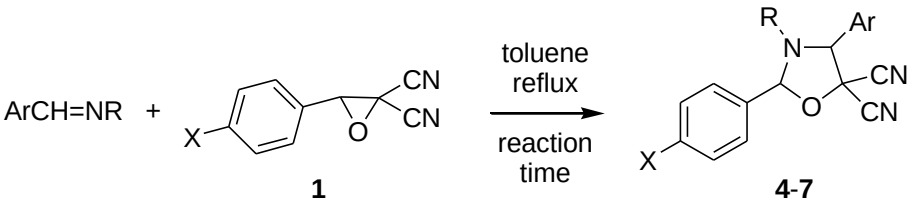
Entry	ArCHO	Epoxide	Conditions[a]	Products, **a**:**b** ratio[b]	Main product, yield
1		**1-H**	● MW, 60 W, rt to 120°C then 45 min at 120°C	**2-H**, 68/32	**2a-H**, 49%
			● toluene, reflux, 35 h	**2-H**, 77/23	**2a-H**, 40%
2		**1-Cl**	● MW, 60 W, rt to 120°C then 40 min at 120°C	**2-Cl**, 71/29	**2a-Cl**, 45%
			● toluene, reflux, 68 h	**2-Cl**, 72/28	**2a-Cl**, 42%
3		**1-OMe**	● MW, 60 W, rt to 80°C then 35 min at 80°C	**2-OMe**, 70/30	**2a-OMe**, 55%
			● toluene, reflux, 45 h	**2-OMe**, 68/32	**2a-OMe**, 52%
4		**1-H**	● MW, 60 W, rt to 120°C then 40 min at 120°C	**3-H**, 66/34	**3a-H**, 25%
			● toluene, reflux, 45 h	**3-H**, 58/42	**3a-H**, 31%
5		**1-Cl**	● MW, 60 W, rt to 120°C then 40 min at 120°C	**3-Cl**, 60/40	**3a-Cl**, 39%
			● toluene, reflux, 72 h	**3-Cl**, 60/40	**3a-Cl**, 28%
6		**1-OMe**	● MW, 60 W, rt to 80°C then 30 min at 80°C	**3-OMe**, 67/33	**3a-OMe**, 40%
			● toluene, reflux, 48 h	**3-OMe**, 71/29	**3a-OMe**, 54%

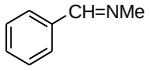
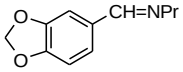
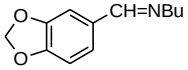
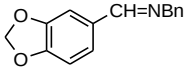
[a] For more detailed conditions, see the experimental part.
[b] Determined from the ^{1}H NMR spectra of the crude mixture.

We next turned our attention to reactions between a series of imines and the oxiranes **1** (X = H, Cl, OMe, NO_2), and attempted both methods.

Using classical heating at toluene reflux, the oxazolidines **4**-**7** were isolated in medium to high yields, except with quite unreactive epoxide **1-NO$_2$**. The reactivity of the epoxide again depends on the electron-donating ability of X, and varies in the order **1-OMe** >> **1-H** ~ **1-Cl** >> **1-NO$_2$**.[2b,f] (Table 2).

Table 2. Reactions between imines and epoxides to give 1,3-oxazolidines

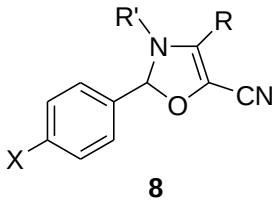


Entry	ArCH=NR	Epoxide	Reaction time	Product, yield
1		**1-H**	24 h	**4a**, 52%
2		**1-Cl**	20 h	**4b**, 60%
3		**1-OMe**	5 h	**4c**, 78%
4		**1-NO$_2$**	35 h	**4d**, 40%
5		**1-H**	27 h	**5a**, 48%
6		**1-Cl**	25 h	**5b**, 59%
7		**1-OMe**	9 h	**5c**, 60%
8		**1-NO$_2$**	45 h	**5d**, 35%
9		**1-H**	32 h	**6a**, 56%
10		**1-Cl**	32 h	**6b**, 59%
11		**1-OMe**	9 h	**6c**, 60%
12		**1-NO$_2$**	65 h	**6d**, 18%
13		**1-H**	40 h	**7a**, 60%
14		**1-Cl**	37 h	**7b**, 50%
15		**1-OMe**	18 h	**7c**, 80%
16		**1-NO$_2$**	72 h	**7d**, 27%

As previously reported with benzylidene anilines as imines,[2b,f] the ^{1}H NMR spectral analysis shows one diastereoisomer is predominantly formed (its relative configuration was not determined), with diastereoisomeric ratios varying from 90:10 to 100:0.

Using microwave irradiation without solvent, the expected oxazolidines **4**-**7** were also formed but rapidly converted to the corresponding 2,3,4-trisubstituted 2,3-dihydrooxazole-5-carbonitriles **8**. The attempts to reduce the formation of the unsaturated derivative **8** by

reducing the reaction time or the irradiation power resulted in lower amounts of **8** but with recovery of starting materials.



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3. Conclusion

We have synthesized novel 1,3-dioxolanes using 1,3-dipolar cycloaddition of aldehydes with carbonyl ylides generated from epoxides, taking advantage of microwave irradiation under solvent-free conditions.

Concerning the reactions of imines with the same carbonyl ylides, the classical heating was preferred for the synthesis of novel 1,3-oxazolidines, since the compounds formed proved unstable under microwave irradiation. The synthesis of 2,3,4-trisubstituted 2,3-dihydrooxazole-5-carbonitriles under microwave irradiation will soon be investigated.

4. Experimental

4.1. General

Melting points were measured on a Kofler apparatus. NMR spectra were recorded with a Bruker ARX 200 P or a Bruker AC 300 P spectrometer (^{1}H at 200 or 300 MHz, respectively, and ^{13}C at 50 or 75 MHz, respectively). Mass spectra (HRMS) were recorded with a Varian MAT 311 spectrometer. Microwave reactions were performed in open glass containers (Prolabo Synthewave® 402) with accurate control of power (maximum power: 300 W) and temperature (by infrared detection).

Starting materials.

Oxiranes[6] and imines[7] were prepared according to described procedures. Toluene was distilled before use. Reactions were performed under dry argon. Petrol refers to petroleum ether (bp 40–60°C).

4.2. General procedures 1 and 2:

General procedure 1: A mixture of epoxide (2.0 mmol) and aldehyde (2.0 mmol) was heated in a microwave oven (power, temperature and time are given in the product description). The residue was purified as specified in the product description.

General procedure 2: A mixture of epoxide (2.0 mmol) and aldehyde (2.0 mmol) in dry toluene (30 mL) was heated at reflux under N_2. The mixture was then evaporated to dryness and purified as specified in the product description.

4.2.1. 2-Phenyl-4-(3,4,5-trimethoxyphenyl)-1,3-dioxolane-5,5-dicarbonitrile (2-H). The general procedure 1 (60 W, 9 min to reach 100°C, 12 min to reach 120°C, and 45 min at 120°C), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and 3,4,5-trimethoxybenzaldehyde (0.39 g), gave a 68/32 mixture from which the preponderant diastereoisomer **2a-H** was isolated by recrystallization from petrol/Et_2O 85:15 in 49% yield as a beige powder: mp 122°C; ^{1}H NMR ($(CD_3)_2CO$) δ 3.83 (s, 3H), 3.93 (s, 6H), 6.04 (s, 1H), 6.59 (s, 1H), 7.03 (s, 2H), 7.61 (m, 3H), 7.77 (m, 2H); ^{13}C NMR ($(CD_3)_2CO$) δ 56.7 (p), 60.7 (p), 70.8 (q), 87.9 (t), 104.8 (t, 2C), 108.5 (t), 113.1 (q), 113.4 (t), 126.4 (q), 128.4 (t, 2C), 129.8 (t, 2C), 132.0 (t), 134.3 (q), 141.0 (q), 155.0 (q, 2C); HRMS, *m*/*z*: 366.1189 found (calcd for $C_{20}H_{18}N_2O_5$, $M^{+\bullet}$ requires: 366.1216). The minor diastereoisomer **2b-H** was identified by the ^{1}H NMR spectra of the crude mixture: ^{1}H NMR ($(CD_3)_2CO$) δ 3.83 (s, 3H), 3.93 (s, 6H), 5.94 (s, 1H), 6.98 (s, 1H), 7.03 (s, 2H), 7.61 (m, 3H), 7.77 (m, 2H). The general procedure 2 (reflux of 53 h), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and 3,4,5-trimethoxybenzaldehyde (0.39 g), gave a 77/23 mixture from which the preponderant diastereoisomer **2a-H** was isolated by recrystallization from petrol/Et_2O 85:15 in 40% yield.

4.2.2. 2-(4-Chlorophenyl)-4-(3,4,5-trimethoxyphenyl)-1,3-dioxolane-5,5-dicarbonitrile (2-Cl). The general procedure 1 (60 W, 9 min to reach 100°C, 12 min to reach 120°C, and 40 min at 120°C), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and 3,4,5-trimethoxybenzaldehyde (0.39 g), gave a 71/29 mixture from which the preponderant diastereoisomer **2a-Cl** was isolated by recrystallization from petrol/Et_2O 85:15 in 45% yield as a white powder: mp 123°C; ^{1}H NMR ($(CD_3)_2CO$) δ 3.80 (s, 3H), 3.89 (s, 6H), 6.00 (s, 1H), 6.57 (s, 1H), 6.99 (s, 2H), 7.60 (d, 2H, *J*=8.4 Hz), 7.74 (d, 2H, *J*=8.4 Hz); ^{13}C NMR

($(CD_3)_2CO$) δ 56.7 (p, 2C), 60.7 (p), 70.8 (q), 87.9 (t), 104.9 (t, 2C), 107.6 (t), 112.9 (q), 113.3 (q), 126.2 (q), 130.0 (t, 2C), 130.1 (t, 2C), 133.1 (q), 137.4 (q), 141.0 (q), 155.0 (q, 2C); HRMS, *m*/*z*: 400.0830 found (calcd for $C_{20}H_{17}N_2O_5{}^{35}Cl$, $M^{+\bullet}$ requires: 400.0826). The minor diastereoisomer **2b-Cl** was identified by the ^1H NMR spectra of the crude mixture: ^1H NMR ($(CD_3)_2CO$) δ 3.83 (s, 3H), 3.91 (s, 6H), 5.92 (s, 1H), 6.96 (s, 1H), 7.02 (s, 2H), 7.6 (4H); ^1H NMR ($CDCl_3$) δ 4.03 (s, 3H), 4.07 (s, 6H), 5.43 (s, 1H), 6.84 (s, 1H), 6.89 (s, 2H), 7.5 (4H). The general procedure 2 (reflux of 68 h), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and 3,4,5-trimethoxybenzaldehyde (0.39 g), gave a 72/28 mixture from which the preponderant diastereoisomer **2a-Cl** was isolated by recrystallization from petrol/Et_2O 85:15 in 42% yield.

4.2.3. 2-(4-Methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,3-dioxolane-5,5-dicarbonitrile (2-OMe). The general procedure 1 (60 W, 3 min to reach 60°C, 6 min to reach 80°C, and 35 min at 80°C), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and 3,4,5-trimethoxybenzaldehyde (0.39 g), gave a 70/30 mixture from which the preponderant diastereoisomer **2a-OMe** was isolated by recrystallization from petrol/Et_2O 85:15 in 55% yield as a white powder: mp 110°C; ^1H NMR ($(CD_3)_2CO$) δ 3.82 (s, 3H), 3.91 (s, 3H), 3.93 (s, 6H), 5.99 (s, 1H), 6.53 (s, 1H), 7.02 (s, 2H), 7.13 (d, 2H, *J*=8.8 Hz), 7.68 (d, 2H, *J*=8.8 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 55.8 (p), 56.6 (p, 2C), 60.7 (p), 70.7 (q), 87.7 (t), 104.8 (t, 2C), 108.7 (t), 113.1 (q), 113.5 (q), 115.1 (t, 2C), 126.1 (q), 126.6 (q), 129.0 (q), 130.1 (t, 2C), 155.0 (q, 2C), 162.8 (q); HRMS, *m*/*z*: 396.1356 found (calcd for $C_{21}H_{20}N_2O_6$, $M^{+\bullet}$ requires: 396.1321). The minor diastereoisomer **2b-OMe** was identified by the ^1H NMR spectra of the crude mixture: ^1H NMR ($(CD_3)_2CO$) δ 3.86 (s, 3H), 3.89 (s, 3H), 3.95 (s, 6H), 5.96 (s, 1H), 6.89 (s, 1H), 7.02 (s, 2H), 7.13 (d, 2H, *J*=8.8 Hz), 7.68 (d, 2H, *J*=8.8 Hz). The general procedure 2 (reflux of 45 h), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and 3,4,5-trimethoxybenzaldehyde (0.39 g), gave a 68/32 mixture from which the preponderant diastereoisomer **2a-OMe** was isolated by recrystallization from petrol/Et_2O 85:15 in 52% yield.

4.2.4. 4-(1,3-Benzodioxol-5-yl)-2-phenyl-1,3-dioxolane-5,5-dicarbonitrile (3-H). The general procedure 1 (60 W, 6 min to reach 100°C, 9 min to reach 120°C, and 40 min at 120°C), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and piperonal (0.30 g), gave a 66/34 mixture from which the preponderant diastereoisomer **3a-H** was isolated by

recristallization from petrol/Et_2O 80:20 in 25% yield as a whitish powder: mp 126°C; ^1H NMR ($(CD_3)_2CO$) δ 6.04 (s, 1H), 6.17 (s, 2H), 6.58 (s, 1H), 7.08 (d, 1H, *J*=7.7 Hz), 7.23 (s, 1H), 7.25 (d, 1H, *J*=7.6 Hz), 7.60 (m, 3H), 7.76 (m, 2H); ^{13}C NMR ($(CD_3)_2CO$) δ 70.8 (q), 87.7 (t), 102.9 (s), 107.3 (t), 108.5 (t), 109.6 (t), 113.0 (q), 113.4 (q), 121.8 (t), 124.7 (q), 128.4 (t, 2C), 129.8 (t, 2C), 132.0 (t), 134.3 (q), 149.4 (q), 150.6 (q); HRMS, *m*/*z*: 320.0774 found (calcd for $C_{18}H_{12}N_2O_4$, $M^{+\bullet}$ requires: 320.0797). The minor diastereoisomer **3b-H** was identified by the ^1H NMR spectra of the crude mixture: ^1H NMR ($(CD_3)_2CO$) δ 5.96 (s, 1H), 6.17 (s, 2H), 6.95 (s, 1H), 7.08 (d, 1H, *J*=7.7 Hz), 7.23 (s, 1H), 7.25 (d, 1H, *J*=7.6 Hz), 7.60 (m, 3H), 7.76 (m, 2H). The general procedure 2 (reflux of 96 h), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and piperonal (0.30 g), gave a 58/42 mixture from which the preponderant diastereoisomer **3a-H** was isolated by recrystallization from petrol/Et_2O 80:20 in 31% yield.

4.2.5. 4-(1,3-Benzodioxol-5-yl)-2-(4-chlorophenyl)-1,3-dioxolane-5,5-dicarbonitrile (3-Cl). The general procedure 1 (60 W, 6 min to reach 100°C, 9 min to reach 120°C, and 40 min at 120°C), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and piperonal (0.30 g), gave a 60/40 mixture from which the preponderant diastereoisomer **3a-Cl** was isolated by recristallization from petrol/Et_2O 80:20 in 39% yield as a white powder: mp 130°C; ^1H NMR ($(CD_3)_2CO$) δ 6.05 (s, 1H), 6.16 (s, 2H), 6.60 (s, 1H), 7.07 (d, 1H, *J*=8.6 Hz), 7.23 (s, 1H), 7.24 (d, 1H, *J*=7.1 Hz), 7.65 (d, 2H, *J*=8.5 Hz), 7.79 (d, 2H, *J*=8.5 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 70.8 (q), 87.8 (t), 102.9 (s), 107.3 (t), 107.5 (t), 109.6 (t), 112.9 (q), 113.3 (q), 121.8 (t), 124.5 (q), 130.0 (t, 2C), 130.2 (t, 2C), 133.2 (q), 137.4 (q), 149.4 (q), 150.6 (q); HRMS, *m*/*z*: 354.0406 found (calcd for $C_{18}H_{11}N_2O_4{}^{35}Cl$, $M^{+\bullet}$ requires: 354.0407). The minor diastereoisomer **3b-Cl** was identified by the ^1H NMR spectra of the crude mixture: ^1H NMR ($(CD_3)_2CO$) δ 5.98 (s, 1H), 6.16 (s, 2H), 6.97 (s, 1H), 7.07 (d, 1H, *J*=8.6 Hz), 7.23 (s, 1H), 7.24 (d, 1H, *J*=7.1 Hz), 7.65 (d, 2H, *J*=8.5 Hz), 7.79 (d, 2H, *J*=8.5 Hz). The general procedure 2 (reflux of 72 h), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and piperonal (0.30 g), gave a 60/40 mixture from which the preponderant diastereoisomer **3a-Cl** was isolated by recrystallization from petrol/Et_2O 80:20 in 28% yield.

4.2.6. 4-(1,3-Benzodioxol-5-yl)-2-(4-methoxyphenyl)-1,3-dioxolane-5,5-dicarbonitrile (3-OMe). The general procedure 1 (60 W, 3 min to reach 60°C, 6 min to reach 80°C, and 30 min at 80°C), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and

piperonal (0.30 g), gave a 67/33 mixture from which the preponderant diastereoisomer **3a-OMe** was isolated by recristallization from petrol/Et_2O 80:20 in 40% yield as a beige powder: mp 137°C; ^{1}H NMR ($(CD_3)_2CO$) δ 3.91 (s, 3H), 5.98 (s, 1H), 6.16 (s, 2H), 6.51 (s, 1H), 7.15 (m, 5H), 7.67 (d, 2H, *J*=6.7 Hz); ^{13}C NMR ($(CD_3)_2CO$) δ 55.8 (p), 70.7 (q), 87.5 (t), 102.9 (s), 107.3 (t), 108.6 (t), 109.6 (t), 112.9 (q), 113.3 (q), 115.1 (t, 2C), 121.7 (t), 124.8 (q), 126.1 (q), 130.1 (t, 2C), 149.4 (q), 150.5 (q), 162.8 (q); HRMS, *m*/*z*: 350.0910 found (calcd for $C_{19}H_{14}N_2O_5$, $M^{+\bullet}$ requires: 350.0903). The minor diastereoisomer **3b-OMe** was identified by the ^{1}H NMR spectra of the crude mixture: ^{1}H NMR ($(CD_3)_2CO$) δ 3.88 (s, 3H), 5.98 (s, 1H), 6.16 (s, 2H), 6.87 (s, 1H), 7.15 (m, 5H), 7.67 (d, 2H, *J*=6.7 Hz). The general procedure 2 (reflux of 48 h), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and piperonal (0.30 g), gave a 71/29 mixture from which the preponderant diastereoisomer **3a-OMe** was isolated by recrystallization from petrol/Et_2O 80:20 in 54% yield.

4.3. General procedure 3: A mixture of epoxide (2.0 mmol) and imine (2.0 mmol) in dry toluene (30 mL) was heated at reflux under N_2. The mixture was then evaporated to dryness. The residue was dissolved in a minimum of Et_2O. Upon addition of petrol, the precipitate formed was collected by filtration before recrystallization from Et_2O.

4.3.1. 3-Methyl-2,4-diphenyl-1,3-oxazolidine-5,5-dicarbonitrile (4a). The general procedure 3 (reflux of 24 h), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and *N*-[phenylmethylene]methanamine (0.24 g), gave 52% of **4a** as a brown powder: mp 128°C; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 4.27 (s, 1H), 5.12 (s, 1H), 7.6 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 34.2 (p), 71.3 (q), 77.4 (t), 100.8 (t), 112.3 (q), 112.8 (q), 128.5 (t, 2C), 128.7 (t, 2C), 128.9 (t, 2C), 129.4 (t, 2C), 129.7 (q), 130.7 (t), 130.8 (t), 134.7 (q); HRMS, *m*/*z*: 288.1133 found (calcd for $C_{18}H_{14}N_3O$, $[M-H]^{+\bullet}$ requires: 288.1133).

4.3.2. 2-(4-Chlorophenyl)-3-methyl-4-phenyl-1,3-oxazolidine-5,5-dicarbonitrile (4b). The general procedure 3 (reflux of 20 h), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and *N*-[phenylmethylene]methanamine (0.24 g), gave 60% of **4b** as a brown glitter: mp 114°C; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3H), 4.31 (s, 1H), 5.14 (s, 1H), 7.6 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 30.9 (p), 71.2 (q), 77.3 (t), 99.9 (t), 112.2 (q), 112.6 (q), 128.5 (t, 2C), 129.2 (t, 2C), 129.4 (q), 129.5 (t, 2C), 130.0 (t, 2C), 130.8 (t), 133.3 (q), 136.8 (q); HRMS, *m*/*z*: 322.0739 found (calcd for $C_{18}H_{13}{}^{35}ClN_3O$, $[M-H]^{+\bullet}$ requires: 322.0747).

4.3.3. 2-(4-Methoxyphenyl)-3-methyl-4-phenyl-1,3-oxazolidine-5,5-dicarbonitrile (4c). The general procedure 3 (reflux of 5 h), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and *N*-[phenylmethylene]methanamine (0.24 g), gave 78% of **4c** as a yellow glitter: mp 149°C; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H), 3.86 (s, 3H), 4.24 (s, 1H), 5.08 (s, 1H), 6.99 (d, 2H, *J*=8.7 Hz), 7.6 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 34.3 (p), 55.4 (p), 71.0 (q), 77.3 (t), 100.6 (t), 112.4 (q), 112.9 (q), 114.3 (t, 2C), 126.6 (q), 128.5 (t, 2C), 129.4 (t, 2C), 129.8 (q), 130.1 (t, 2C), 130.6 (t), 161.5 (q); HRMS, *m*/*z*: 319.1330 found (calcd for $C_{19}H_{17}N_3O_2$, $M^{+\bullet}$ requires: 319.1321).

4.3.4. 3-Methyl-2-(4-nitrophenyl)-4-phenyl-1,3-oxazolidine-5,5-dicarbonitrile (4d). The general procedure 3 (reflux of 35 h), using 3-(4-nitrophenyl)oxirane-2,2-dicarbonitrile (**1-NO_2**, 0.43 g) and *N*-[phenylmethylene]methanamine (0.24 g), gave 40% of **4d** as a beige powder: mp 164°C; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 4.38 (s, 1H), 5.22 (s, 1H), 7.6 (m, 5H), 7.82 (d, 2H, *J*=8.7 Hz), 8.36 (d, 2H, *J*=8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 34.2 (p), 71.4 (q), 77.3 (t), 99.0 (t), 111.9 (q), 112.3 (q), 124.2 (t, 2C), 128.4 (t, 2C), 128.6 (q), 128.9 (q), 129.6 (t, 2C), 129.7 (t, 2C), 131.0 (t), 141.5 (q); HRMS, *m*/*z*: 333.0995 found (calcd for $C_{18}H_{13}N_4O_3$, $[M-H]^{+\bullet}$ requires: 333.0988).

4.3.5. 4-(1,3-Benzodioxol-5-yl)-2-phenyl-3-propyl-1,3-oxazolidine-5,5-dicarbonitrile (5a). The general procedure 3 (reflux of 27 h), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and *N*-[1,3-benzodioxol-5-ylmethylene]propylamine (0.38 g), gave 48% of **5a** as a beige glitter: mp 101°C; ^{1}H NMR ($CDCl_3$) δ 0.66 (t, 3H, *J*=7.3 Hz), 1.05 (n, 2H, *J*=7.3 Hz), 2.55 (m, 2H), 4.41 (s, 1H), 5.33 (s, 1H), 6.05 (s, 2H), 6.91 (d, 1H, *J*=8.0 Hz), 7.12 (dd, 1H, *J*=8.0 and 1.5 Hz), 7.19 (d, 1H, *J*=1.5 Hz), 7.5 (m, 3H), 7.6 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.6 (p), 18.9 (s), 49.9 (s), 71.2 (q), 75.5 (t), 99.2 (t), 101.7 (s), 108.4 (t), 108.9 (t), 112.5 (q), 112.9 (q), 122.9 (t), 123.7 (q), 128.7 (t, 2C), 128.8 (t, 2C), 130.6 (t), 135.9 (q), 148.5 (q), 149.5 (q); HRMS, *m*/*z*: 361.1421 found (calcd for $C_{21}H_{19}N_3O_3$, $M^{+\bullet}$ requires: 361.1426).

4.3.6. 4-(1,3-Benzodioxol-5-yl)-2-(4-chlorophenyl)-3-propyl-1,3-oxazolidine-5,5-dicarbonitrile (5b). The general procedure 3 (reflux of 25 h), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and *N*-[1,3-benzodioxol-5-ylmethylene]propylamine (0.38 g), gave 59% of **5b** as a beige powder: mp 140°C; ^{1}H NMR

($CDCl_3$) δ 0.64 (t, 3H, *J*=7.3 Hz), 1.11 (n, 2H, *J*=7.2 Hz), 2.52 (m, 2H), 4.41 (s, 1H), 5.31 (s, 1H), 6.06 (s, 2H), 6.91 (d, 1H, *J*=8.0 Hz), 7.11 (dd, 1H, *J*=8.0 and 1.7 Hz), 7.16 (d, 1H, *J*=1.6 Hz), 7.44 (d, 2H, *J*=8.5 Hz), 7.56 (d, 2H, *J*=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 11.6 (p), 19.1 (s), 50.0 (s), 71.1 (q), 75.5 (t), 98.4 (t), 101.7 (s), 108.3 (t), 108.9 (t), 112.4 (q), 112.7 (q), 122.9 (t), 123.4 (q), 129.2 (t, 2C), 130.0 (t, 2C), 134.6 (q), 136.6 (q), 148.6 (q), 149.6 (q); HRMS, *m*/*z*: 315.1013 found (calcd for $C_{18}H_{18}{}^{35}ClNO_2$, $[M\text{-}OC(CN)_2]^{+\bullet}$ requires: 315.1026).

4.3.7. 4-(1,3-Benzodioxol-5-yl)-2-(4-methoxyphenyl)-3-propyl-1,3-oxazolidine-5,5-dicarbonitrile (5c). The general procedure 3 (reflux of 9 h), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and *N*-[1,3-benzodioxol-5-ylmethylene]propylamine (0.38 g), gave 60% of **5c** as yellow needles: mp 138°C; ^{1}H NMR ($CDCl_3$) δ 0.65 (t, 3H, *J*=7.3 Hz), 1.07 (n, 2H, *J*=7.3 Hz), 2.49 (m, 2H), 3.85 (s, 3H), 4.41 (s, 1H), 5.31 (s, 1H), 6.05 (s, 2H), 6.5 (m, 3H), 7.11 (dd, 1H, *J*=8.0 and 1.7 Hz), 7.18 (d, 1H, *J*=1.6 Hz), 7.5 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.7 (p), 18.9 (s), 50.0 (s), 55.4 (p), 71.0 (q), 75.5 (t), 99.1 (t), 101.7 (s), 108.4 (t), 108.9 (t), 112.7 (q), 113.0 (q), 114.2 (t, 2C), 122.9 (t), 123.9 (q), 127.9 (q), 130.1 (t, 2C), 148.5 (q), 149.5 (q), 161.4 (q); HRMS, *m*/*z*: 311.1526 found (calcd for $C_{19}H_{21}NO_3$, $[M\text{-}OC(CN)_2]^{+\bullet}$ requires: 311.1521).

4.3.8. 4-(1,3-Benzodioxol-5-yl)-2-(4-nitrophenyl)-3-propyl-1,3-oxazolidine-5,5-dicarbonitrile (5d). The general procedure 3 (reflux of 45 h), using 3-(4-nitrophenyl)oxirane-2,2-dicarbonitrile (**1-NO$_2$**, 0.43 g) and *N*-[1,3-benzodioxol-5-ylmethylene]propylamine (0.38 g), gave 35% of **5d** as a beige powder: mp 178°C; ^{1}H NMR ($CDCl_3$) δ 0.65 (t, 3H, *J*=7.3 Hz), 1.11 (n, 2H, *J*=7.6 Hz), 2.55 (m, 2H), 4.46 (s, 1H), 5.44 (s, 1H), 6.07 (s, 2H), 6.93 (d, 1H, *J*=7.9 Hz), 7.12 (dd, 1H, *J*=8.0 and 1.6 Hz), 7.16 (s, 1H), 7.82 (d, 2H, *J*=8.7 Hz), 8.34 (d, 2H, *J*=8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 11.6 (p), 19.4 (s), 50.2 (s), 71.3 (q), 75.7 (t), 97.6 (t), 101.8 (s), 108.2 (t), 109.0 (t), 112.2 (q), 112.4 (q), 122.9 (t), 122.9 (q), 124.1 (t, 2C), 128.0 (q), 129.7 (t, 2C), 142.9 (q), 148.7 (q),149.8 (q); HRMS, *m*/*z*: 406.1260 found (calcd for $C_{21}H_{18}N_4O_5$, $M^{+\bullet}$ requires: 406.1277).

4.3.9. 4-(1,3-Benzodioxol-5-yl)-3-butyl-2-phenyl-1,3-oxazolidine-5,5-dicarbonitrile (6a). The general procedure 3 (reflux of 32 h), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and *N*-[1,3-benzodioxol-5-ylmethylene]butylamine (0.41 g), gave 56% of **6a** as a beige glitter: mp 107°C; ^{1}H NMR ($CDCl_3$) δ 0.66 (t, 3H, *J*=6.8 Hz), 1.05 (m, 4H), 2.55 (m, 2H),

4.41 (s, 1H), 5.33 (s, 1H), 6.05 (s, 2H), 6.91 (d, 1H, *J*=8.0 Hz), 7.12 (d, 1H, *J*=8.0 Hz), 7.18 (d, 1H, *J*=1.5 Hz), 7.5 (m, 3H), 7.6 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6 (p), 20.2 (s), 27.3 (s), 47.6 (s), 71.2 (q), 75.4 (t), 99.1 (t), 101.7 (s), 108.4 (t), 108.9 (t), 112.5 (q), 112.9 (q), 122.9 (t), 123.7 (q), 128.7 (t, 2C), 128.8 (t, 2C), 130.6 (t), 135.9 (q), 148.5 (q), 149.5 (q); HRMS, *m*/*z*: 375.1573 found (calcd for $C_{22}H_{21}N_3O_3$, $M^{+\bullet}$ requires: 375.1583).

4.3.10. 4-(1,3-Benzodioxol-5-yl)-3-butyl-2-(4-chlorophenyl)-1,3-oxazolidine-5,5-dicarbonitrile (6b). The general procedure 3 (reflux of 32 h), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and *N*-[1,3-benzodioxol-5-ylmethylene]butylamine (0.41 g), gave 59% of **6b** as a pale yellow powder: mp 138°C; ^{1}H NMR ($CDCl_3$) δ 0.67 (t, 3H, *J*=6.8 Hz), 1.05 (m, 4H), 2.57 (m, 2H), 4.40 (s, 1H), 5.31 (s, 1H), 6.05 (s, 2H), 6.91 (d, 1H, *J*=7.9 Hz), 7.11 (dd, 1H, *J*=8.0 and 1.6 Hz), 7.15 (d, 1H, *J*=1.4 Hz), 7.44 (d, 2H, *J*=6.7 Hz), 7.56 (d, 2H, *J*=6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.5 (p), 20.2 (s), 27.4 (s), 47.7 (s), 71.1 (q), 75.3 (t), 98.2 (t), 101.7 (s), 108.3 (t), 108.9 (t), 112.5 (q), 112.7 (q), 122.9 (t), 123.4 (q), 129.1 (t, 2C), 130.0 (t, 2C), 134.6 (q), 136.6 (q), 148.6 (q), 149.6 (q); HRMS, *m*/*z*: 329.1197 found (calcd for $C_{19}H_{20}{}^{35}ClNO_2$, $[M\text{-}OC(CN)_2]^{+\bullet}$ requires: 329.1183).

4.3.11. 4-(1,3-Benzodioxol-5-yl)-3-butyl-2-(4-methoxyphenyl)-1,3-oxazolidine-5,5-dicarbonitrile (6c). The general procedure 3 (reflux of 9 h), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and *N*-[1,3-benzodioxol-5-ylmethylene]butylamine (0.41 g), gave 60% of **6c** as orange needles: mp 114°C; ^{1}H NMR ($CDCl_3$) δ 0.65 (t, 3H, *J*=6.8 Hz), 1.05 (m, 4H), 2.56 (m, 2H), 3.86 (s, 3H), 4.38 (s, 1H), 5.29 (s, 1H), 6.05 (s, 2H), 6.91 (d, 1H, *J*=8.0 Hz), 6.97 (d, 2H, *J*=8.7 Hz), 7.11 (dd, 1H, *J*=8.0 and 1.5 Hz), 7.17 (d, 1H, *J*=1.5 Hz), 7.53 (d, 2H, *J*=8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.6 (p), 20.3 (s), 27.2 (s), 47.6 (s), 55.4 (p), 71.0 (q), 75.3 (t), 98.9 (t), 101.7 (s), 108.4 (t), 108.9 (t), 112.6 (q), 113.0 (q), 114.2 (t, 2C), 122.9 (t), 123.8 (q), 127.9 (q), 130.1 (t, 2C), 148.5 (q), 149.5 (q), 161.4 (q); HRMS, *m*/*z*: 378.1597 found (calcd for $C_{22}H_{22}N_2O_4$, $[M\text{-}HCN]^{+\bullet}$ requires: 378.1580).

4.3.12. 4-(1,3-Benzodioxol-5-yl)-3-butyl-2-(4-nitrophenyl)-1,3-oxazolidine-5,5-dicarbonitrile (6d). The general procedure 3 (reflux of 65 h), using 3-(4-nitrophenyl)oxirane-2,2-dicarbonitrile (**1-NO$_2$,** 0.43 g) and *N*-[1,3-benzodioxol-5-ylmethylene]butylamine (0.41 g), gave 18% of **6d** as an orange powder: mp 126°C; ^{1}H NMR ($CDCl_3$) δ 0.66 (t, 3H, *J*=6.8

Hz), 1.05 (m, 4H), 2.57 (m, 2H), 4.45 (s, 1H), 5.43 (s, 1H), 6.06 (s, 2H), 6.92 (d, 1H, *J*=7.9 Hz), 7.10 (dd, 1H, *J*=8.1 and 1.6 Hz), 7.14 (d, 1H, *J*=1.6 Hz), 7.81 (d, 2H, *J*=8.8 Hz), 8.33 (d, 2H, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.5 (p), 20.2 (s), 27.7 (s), 47.9 (s), 71.3 (q), 75.5 (t), 97.4 (t), 101.8 (s), 108.2 (t), 109.0 (t), 112.2 (q), 112.4 (q), 122.9 (t), 124.1 (t, 2C), 128.0 (q), 129.7 (t, 2C), 142.9 (q), 148.7 (q), 149.3 (q), 149.8 (q); HRMS, *m*/*z*: 420.1457 found (calcd for $C_{22}H_{20}N_4O_5$, $M^{+\bullet}$ requires: 420.1434).

4.3.13. 4-(1,3-Benzodioxol-5-yl)-3-benzyl-2-phenyl-1,3-oxazolidine-5,5-dicarbonitrile (7a). The general procedure 3 (reflux of 40 h), using 3-phenyloxirane-2,2-dicarbonitrile (**1-H**, 0.34 g) and *N*-[1,3-benzodioxol-5-ylmethylene]benzylamine (0.48 g), gave 60% of **7a** as a beige glitter: mp 132°C; ^{1}H NMR ($CDCl_3$) δ 3.64 (d, 1H, *J*=15 Hz), 3.86 (d, 1H, *J*=15 Hz), 4.28 (s, 1H), 5.25 (s, 1H), 6.08 (s, 2H), 6.87 (m, 2H), 6.97 (d, 1H, *J*=7.8 Hz), 7.17 (d, 1H, *J*=8.1 Hz), 7.3 (m, 4H), 7.6 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 49.2 (s), 70.8 (q), 72.7 (t), 96.4 (t), 101.8 (s), 108.6 (t), 109.1 (t), 112.7 (q), 112.8 (q), 122.8 (t), 123.2 (q), 128.3 (t), 128.5 (t, 2C), 128.9 (t, 2C), 129.2 (t, 2C), 130.1 (t, 2C), 130.8 (t), 131.4 (q), 134.6 (q), 148.7 (q), 149.6 (q); HRMS, *m*/*z*: 329.1426 found (calcd for $C_{22}H_{19}NO_2$, $[M\text{-}CO(CN)_2]^{+\bullet}$ requires: 329.1416).

4.3.14. 4-(1,3-Benzodioxol-5-yl)-3-benzyl-2-(4-chlorophenyl)-1,3-oxazolidine-5,5-dicarbonitrile (7b). The general procedure 3 (reflux of 37 h), using 3-(4-chlorophenyl)oxirane-2,2-dicarbonitrile (**1-Cl**, 0.41 g) and *N*-[1,3-benzodioxol-5-ylmethylene]benzylamine (0.48 g), gave 50% of **7b** as a white powder: mp 147°C; ^{1}H NMR ($CDCl_3$) δ 3.63 (d, 1H, *J*=15 Hz), 3.85 (d, 1H, *J*=15 Hz), 4.28 (s, 1H), 5.22 (s, 1H), 6.09 (s, 2H), 6.84 (m, 2H), 6.98 (d, 1H, *J*=7.9 Hz), 7.2 (m, 5H), 7.46 (d, 2H, *J*=8.4 Hz), 7.58 (d, 2H, *J*=8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 49.5 (s), 70.8 (q), 72.9 (t), 95.7 (t), 101.8 (s), 108.6 (t), 109.2 (t), 112.6 (q), 112.6 (q), 122.6 (t), 123.2 (q), 128.4 (t), 128.6 (t, 2C), 129.3 (t, 2C), 130.0 (t, 2C), 130.5 (t, 2C), 131.4 (q), 133.2 (q), 136.7 (q), 148.8 (q), 149.7 (q); HRMS, *m*/*z*: 363.1040 found (calcd for $C_{22}H_{18}NO_2{}^{35}Cl$, $M^{+\bullet}$ requires: 363.1026).

4.3.15. 4-(1,3-Benzodioxol-5-yl)-3-benzyl-2-(4-methoxyphenyl)-1,3-oxazolidine-5,5-dicarbonitrile (7c). The general procedure 3 (reflux of 18 h), using 3-(4-methoxyphenyl)oxirane-2,2-dicarbonitrile (**1-OMe**, 0.40 g) and *N*-[1,3-benzodioxol-5-ylmethylene]benzylamine (0.48 g), gave 80% of **7c** as pale yellow needles: mp 116°C; ^{1}H NMR ($CDCl_3$) δ 3.63 (d, 1H, *J*=15 Hz), 3.86 (d, 1H, *J*=15 Hz), 3.88 (s, 3H), 4.24 (s, 1H),

5.21 (s, 1H), 6.08 (s, 2H), 6.86 (m, 2H), 7.0 (m, 3H), 7.2 (m, 5H), 7.59 (d, 2H, *J*=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 49.1 (s), 55.4 (p), 70.6 (q), 72.5 (t), 96.1 (t), 101.7 (s), 108.6 (t), 109.1 (t), 112.8 (q), 112.9 (q), 114.4 (t, 2C), 122.9 (t), 123.2 (q), 126.4 (q), 128.3 (t), 128.5 (t, 2C), 130.1 (t, 2C), 130.6 (t, 2C), 131.5 (q), 148.7 (q), 149.6 (q), 161.5 (q); HRMS, *m*/*z*: 412.1401 found (calcd for $C_{25}H_{20}N_2O_4$, $[M\text{-}HCN]^{+\bullet}$ requires: 412.1423).

4.3.16. 4-(1,3-Benzodioxol-5-yl)-3-benzyl-2-(4-nitrophenyl)-1,3-oxazolidine-5,5-dicarbonitrile (7d). The general procedure 3 (reflux of 72 h), using 3-(4-nitrophenyl)oxirane-2,2-dicarbonitrile (**1-NO$_2$,** 0.43 g) and *N*-[1,3-benzodioxol-5-ylmethylene]benzylamine (0.48 g), gave 27% of **7d** as a white powder: mp 187°C; ^{1}H NMR ($CDCl_3$) δ 3.70 (d, 1H, *J*=15 Hz), 3.82 (d, 1H, *J*=15 Hz), 4.36 (s, 1H), 5.34 (s, 1H), 6.11 (s, 2H), 6.87 (m, 2H), 7.00 (d, 1H, *J*=8.0 Hz), 7.2 (m, 5H), 7.77 (d, 2H, *J*=8.8 Hz), 8.29 (d, 2H, *J*=8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 50.3 (s), 70.9 (q), 73.6 (t), 95.5 (t), 101.9 (s), 108.4 (t), 109.3 (t), 112.3 (q), 112.4 (q), 122.1 (t), 123.2 (q), 124.0 (t, 2C), 128.6 (t), 128.7 (t, 2C), 129.8 (t, 2C), 130.1 (t, 2C), 131.5 (q), 141.7 (q), 148.9 (q), 149.2 (q), 149.9 (q); HRMS, *m*/*z*: 374.1258 found (calcd for $C_{22}H_{18}N_2O_4$, $[M\text{-}CO(CN)_2]^{+\bullet}$ requires: 374.1267).

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